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mercury compounds. To our knowledge this is the first example in which the product of attack of a carbene on any carbon-metal bond has been isolated as a stable compound.⁴

Although the insertion product II is stable at room temperature, it was found to decompose at higher temperatures to form nearly equimolar amounts of vinyl chloride III and alkylmercuric chloride IV. The reaction has been carried out with R = R' = H; $R = R' = CH_3$; $R = n-C_3H_7$, R' = H; and $R = CH_3$, $R' = C_2H_5$.

$$\begin{array}{c} \operatorname{RR'CHHgCHRR'}_{I} + :\operatorname{CCl}_{2} \xrightarrow{\text{pentane}} \operatorname{RR'CHCCl}_{2}\operatorname{HgCHRR'}_{I} \\ \operatorname{II} \xrightarrow{I} \operatorname{RR'C=CHCl}_{A} + \operatorname{RR'CHHgCl}_{III} \\ \operatorname{III} & \operatorname{IV} \end{array}$$

For example, diisopropylmercury (0.03 mole), b.p. $33-35^{\circ}$ (0.3–0.4 mm.), in pentane was treated with dichlorocarbene generated from ethyl trichloroacetate (0.06 mole) by the method of Parham and Schweizer.⁶ The pentane solution was washed, dried, and evaporated in the usual manner to an oily residue. At no time during the reaction or work-up was any free mercury observed. Upon careful distillation, the crude product yielded a small amount of recovered diisopropylmercury and 57% of the theoretical amount of insertion product V, b.p. $94-95^{\circ}$ (0.3–0.4 mm.); a clear viscous liquid structure was confirmed by its chemical and spectral properties. The infrared spectrum was nearly identical with that of diisopropylmercury. The 60 Mc./sec. n.m.r. spectrum showed two doublets

$$(CH_{3})_{2}CHCCl_{2}HgCH(CH_{3})_{2} \xrightarrow{\Delta} (CH_{3})_{2}C = CHCl + VI$$

$$V \qquad VI \qquad (CH_{3})_{2}CHHgCl$$

VII

at τ 8.63 and 8.79, respectively (J = 7 c.p.s.), which were assigned to the two sets of isopropyl methyl groups. The two tertiary proton multiplets were visible at *ca.* τ 7.3 and 8.1, but were complicated because of noise and the presence of Hg¹⁹⁹ satellite peaks.⁷

That mercury compound V did not arise because of a nucleophilic attack of the trichloromethyl anion on the mercury atom is suggested by the fact that simple dialkylmercury compounds are completely inert to attack by strongly nucleophilic iodide or thiosulfate ions as well as by strong bases such as sodium methoxide.⁹

The thermal decomposition of pure V at $100-120^{\circ}$ resulted in a 1.00:1.09 mole ratio of isopropylmercuric chloride (VI) to 2-methyl-1-chloro-1-propene (VII), each of which was unequivocally identified by melting or boiling point, infrared spectrum, and n.m.r. spectrum. No other products were observed.

Similar dichlorocarbene insertion reactions were carried out on di-sec-butylmercury (I, $R = CH_3$, $R' = C_2H_5$) and di-*n*-butylmercury (I, R = H, $R' = CH_3CH_2CH_2$). In each instance thermal decomposition of the insertion product occurred before it was

(4) Evidence for the insertion of halo carbenes into carbon-alkali metal bonds has been published,³ but the intermediate products which are postulated apparently eliminate alkali metal halide to form a carbene that goes on to produce the observed products.

(5) G. L. Closs and L. E. Closs, J. Am. Chem. Soc., ${\bf 85},$ 99 (1963), and references cited therein.

(6) W. E. Parham and E. E. Schweizer, J. Org. Chem., 24, 1773 (1959).

(7) Two Hg¹⁹⁹ satellite doublets were symmetrically oriented about the large doublet at 8.63 and correspond to $J_{\rm Hg^{199}-H_1} = 165$ c.p.s., a value assigned to the coupling between Hg¹⁹⁹ and the protons on the β -carbon atom.⁸ Thus, the doublet at 8.63 is associated with the isopropyl group directly attached to the mercury atom of V.

(8) R. E. Dessy, T. J. Flautt, H. H. Jaffé, and G. F. Reynolds, J. Chem. Phys., **30**, 1422 (1959).

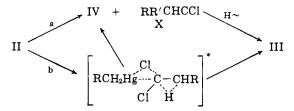
(9) Experimental observations of the authors.

distilled. The product vinyl chlorides VIII and IX were obtained¹⁰ accompanied by the expected alkyl- $CH_{10}C$

mercuric chlorides. A simple test for the alkylmercuric halide¹¹ revealed that it was present only *after* the thermal decomposition had taken place.

The attack of dichlorocarbene on the carbon-mercury bond is not surprising in view of the known susceptibility of dialkylmercury compounds to cleavage by a variety of electrophiles.¹²⁻¹⁴ Further work on the stereochemistry and relative reactivity of various types of carbon-mercury bonds is being carried out to elucidate the nature of the transition state in this reaction.

The thermally induced breakdown of insertion product II is particularly interesting in view of the formal similarity to the decomposition of phenyl(trichloromethyl)mercury to form dichlorocarbene.¹⁵ In analogy with the latter transformation, path a, in which a distinct intermediate carbene (X) is formed and undergoes a subsequent hydrogen migration, for which ample precedent exists,¹⁶ would appear more likely than the concerted path b. Direct evidence for



the intermediacy of carbene X is presently being sought.

(10) Preliminary vapor phase chromatographic data on VIII indicated a mixture of stereoisomers with one in predominance.

(11) Alkylmercuric chlorides form water-soluble thiosulfate salts which can be readily precipitated as the iodide.

(12) F. R. Jensen, J. Am. Chem. Soc., 82, 2469 (1960).

(13) R. E. Dessy, G. F. Reynolds, and J.-Y. Kim, ibid., 81, 2683 (1959).

(14) L. H. Gale, F. R. Jensen, and J. A. Landgrebe, Chem. Ind. (London), 118 (1960).

(15) D. Seyferth, R. J. Minasz, A. J.-H. Treiber, J. A. Burlitch, and S. R. Dowd, J. Org. Chem., 28, 1163 (1963).

(16) L. Friedman and H. Shechter, J. Am. Chem. Soc., 83, 3159 (1961), and references cited therein.

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Synthesis of a Benzocyclopropene Derivative

Sir:

Benzocyclopropene (I) should be intermediate in strain between benzocyclobutene, a stable entity,¹ and benzyne,² which has only been observed³ as a transient species. However, past efforts to obtain I or its derivatives⁴ have been unsuccessful. We now report the preparation of 1,1-dimethyl-3-carbomethoxybenzocyclopropene (II), a crystalline compound of moderate stability.

Methyl 3,3-dimethylindiazene-6-carboxylate⁵ (III,

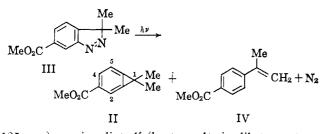
(1) M. P. Cava and D. R. Napier, J. Am. Chem. Soc., 78, 500 (1956); 80, 2255 (1958).

(2) For a review, see R. Huisgen and J. Sauer, Angew. Chem., 72, 91 (1960).

(3) M. Stiles and R. G. Miller, J. Am. Chem. Soc., 82, 3802 (1960);
 R. S. Berry, G. N. Spokes, and M. Stiles, *ibid.*, 84, 3570 (1962).

(4) E. F. Ullman and E. Buncel, *ibid.*, 85, 2106 (1963).

(5) Compound III was prepared (J. M. Muchowski, Ph.D. Thesis. University of Ottawa, 1962) from the N-nitroso derivative of methyl 3-benzamido-4-isopropylbenzoate by Huisgen's procedure for the synthesis of indazoles (R. Huisgen and H. Nakateni, Ann., **573**, 181 (1951)). The longest wave-length absorption band in the ultraviolet spectrum of III occurred at 350 m μ (log ϵ 2.40).



125 mg.) was irradiated⁶ (best results in dilute pentane solution under nitrogen) with ultraviolet light (Hanovia medium-pressure quartz mercury-vapor lamp, 200 w., Pyrex filter) for 10 min. at 20°. The solution was concentrated to 5 ml. and cooled to -70° for several hours. The precipitated solid (ca. 60 mg.) was⁷ largely methyl p-isopropenylbenzoate (IV), m.p. $51-52^{\circ}$. Further concentration of the mother liquors gave crystals of II, which, however, were more or less contaminated with IV. A more satisfactory separation was achieved by rapid chromatography at -5° of the mother liquors over basic alumina (pretreated with diethylamine) and elution with 8:1 pentane-methylene chloride. Crystallization then gave pure II, m.p. $32-32.5^{\circ}$. Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.99; H, 6.82; mol. wt., 176. Found: C, 75.08; H, 6.92; mol. wt. (Rast, in dicyclopentadiene), 163. The ultra-violet absorption spectrum showed λ_{\max}^{MeOH} 238, 279, and 286 m μ (sh); log ϵ 3.95, 3.41, 3.41, and 3.39, respectively. The infrared spectrum (liquid) find showed strong bands at 1725, 1296, 1216, 1097, and $758 \text{ cm}.^{-1}$.

The n.m.r. spectrum (60 Mc./sec.) of II in carbon tetrachloride solution showed the following features given in τ -values (assignments shown in parentheses): 8.38, 6 protons (gem-dimethyl); 6.13, 3 protons (ester methyl); 2.84, quartet, 1 proton (H₅, $J_{ortho} = 6.6$ and $J_{para} = 1.9$ c.p.s.); 2.3, quartet, 1 proton (H₂, $J_{para} = 1.9$ and $J_{meta} = 0.7$ c.p.s.); 2.14, doublet,⁸ 1 proton (H₄, $J_{ortho} = 6.6$ c.p.s.). The assignments of the aromatic bands are based on the known^{9a} low-field shift of aromatic protons ortho to a carbomethoxy group and on the magnitude of J_{ortho} . It is interesting that J_{para} is greater than J_{meta} , the reverse of the usual order, and that J_{ortho} is a little smaller than normal.^{9b} Such variations are not unexpected, as there could be considerable distortion of the benzene ring in II.

The aromatic character (e.g., the ring current effect) of the benzene ring is not greatly disturbed in II, as shown by the normal chemical shifts of protons H_2 , H_4 , and H_5 , as well as by the similarity of the ultraviolet absorption spectrum of II to that of methyl benzoate. The equivalence of the gem-dimethyl protons in the n.m.r. spectrum of II, even at -150° (CCl₂F₂ solution), is consistent with a planar or a rapidly inverting, and therefore presumably nearly planar, structure for the benzocyclopropene skeleton.¹⁰

(6) The preparation of cyclopropenes by irradiation of pyrazolenines has been reported recently: G. L. Closs and W. Böll, Angew. Chem. Intern. Ed. Engl., 2, 399 (1963); G. Ege, Tetrahedron Letters, 1667 (1963).

(9) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy to Organic Chemistry," Pergamon Press, New York, N. Y., 1959: (a) p. 63; (b) p. 85.

(10) The possibility of a nonplanar structure for benzocyclopropene has been discussed by Ullman and Buncel.⁴

Although II is stable for several hours at room temperature, it is completely destroyed in refluxing benzene after 15 min. The compound is very sensitive to acids, but not to bases. The transformation products and the rate of decomposition of II are being investigated; preliminary n.m.r. evidence shows that at least one of the products contains an isopropenyl group.

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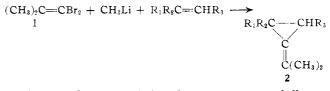
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The Synthesis of Methylenecyclopropanes via an α -Elimination Reaction

Sir:

Methylene carbenes ($R_2C==C$:) have been suggested as intermediates in the formation of butatrienes from exocyclic vinyl halides and sodium amide¹ or phenyllithium.² With simpler 2,2-diaryl vinyl bromides rearrangement occurs to give diaryl acetylenes. Stereochemical evidence has been presented^{3,4} to prove that this reaction does not produce a methylene carbene. The formation of substituted methylenecyclopropanes in low yields by the reaction of vinyl chlorides, olefins, and potassium *t*-butoxide has recently been disclosed.⁵ This reaction is assumed to involve intermediate methylene carbenes.

We have found that aliphatic vinylidene bromides give α -elimination reactions with methyllithium. While 1,1-dibromopropene, methyllithium, and olefins gave methylacetylene; 1,1-dibromo-2-methylpropene (1), methyllithium, and olefins gave moderate yields (12– 70%) of isopropylidenecyclopropanes (2).



The reaction $1 \rightarrow 2$ has been run successfully at -80 to $+60^{\circ}$. A solution of methyllithium in ether was added slowly to an equimolar amount of 1 dissolved in a three- to tenfold excess of olefin. The products were isolated by standard separation and distillation procedures or by preparative scale vapor phase chromatography. The highest yields of 2 were obtained with nucleophilic olefins such as vinyl ethers. The reaction with ethyl isobutenyl ether gave a 59% yield of 2 (R₁ = R₂ = CH₃, R₃ = OCH₂CH₃), b.p. 85° (115 mm.). Anal. Calcd. for C₁₀H₁₈O: C, 77.9; H, 11.8. Found: C, 77.9; H, 12.0. Isopropylidenecyclopropanes were also obtained from ethyl vinyl ether (70%), methyl vinyl ether (60%), cyclohexene (41%), isobutylene (35%), norbornene (22%), 2-methyl-2-butene (12%), and trans-2-butene (23%).

All of the products 2 showed infrared absorption near 5.60 μ which was attributed to the strained double bond exocyclic to the cyclopropane ring. Two common features of the proton magnetic resonance spectra of 2 also assisted in the identification of the products: high-field resonances of the hydrogen atoms on the cyclopropane ring and long-range coupling ($\sim 2 \text{ c.p.s.}$) between the ring hydrogens and the isopropylidene

(1) C. R. Hauser and D. Lednicer, J. Org. Chem., 22, 1248 (1957).

(2) D. Y. Curtin and W. H. Richardson, J. Am. Chem. Soc., 81, 4719 (1959).

(3) A. A. Bothner-By, ibid., 77, 3293 (1955).

(4) D. Y. Curtin, E. W. Flynn, and R. F. Nystrom, *ibid.*, **80**, 4599 (1958).
 (5) M. Tanabe and R. A. Walsh, *ibid.*, **85**, 3522 (1963).

(6) Satisfactory elemental analyses and spectral data were obtained for all these compounds.

⁽⁷⁾ The structure was deduced from the n.m.r. spectrum and was confirmed by comparison of the photolysis product with a sample prepared from methyl p-isopropylbenzoate by bromination with N-bromosuccinimide followed by dehydrobromination. Hydrolysis of IV gave p-isopropenylbenzoic acid, m.p. 160°; G. B. Bachmann, C. L. Carson, and M. Robinson, J. Am. Chem. Soc., **73**, 1964 (1951), report the same melting point for this acid.

⁽⁸⁾ Both components of the doublet were rather broad and thus obscured the small coupling due to J_{mela} which should also be present. This could be due to a very small long-range coupling of, e.g., 0.3 c.p.s. with the gemdimethyl group.